A review of sugarcane bagasse for second-generation bioethanol and biopower production

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Abstract: Sugarcane bagasse is a large-volume agriculture residue that is generated on a ~540 million metric tons per year basis globally[1,2] with the top-three producing countries in Latin America being Brazil (~181 million metric ton yr^{-1}),[3] Mexico (~15 million metric ton yr^{-1}),[4] and Colombia (~7 million metric ton yr^{-1}),[5] respectively.[6] Given sustainability concerns and the need to maximize the utilization of bioresources, the use of sugarcane bagasse is receiving significant attention in biorefining applications, as it is a promising resource for the conversion to biofuels and biopower. This review provides a comprehensive review of bagasse and its chemical constituents and on-going research into its utilization as a feedstock for cellulosic ethanol and electricity generation. © 2016 Society of Chemical Industry and John Wiley & Sons, Ltd

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Introduction

In the past few decades, the high consumption of fossil fuels has led to an increased use of difficult-to-recover petroleum reserves, which have heightened environmental concerns along with energy security issues. These issues, in addition to global climate change due to greenhouse gas (GHG) emissions, have led researchers to explore alternative fuels based on sustainable bioresources. Agro-energy crops and plant residues are two of the most promising low-cost, sustainable biomaterials for biofuel and power generation.

First-generation bioethanol has been widely used for vehicle fuels, lowering net carbon dioxide emissions compared to fossil fuels. However, the increasing demand for first generation ethanol requires high feedstock production, leading to food vs. fuel concerns and an increase in land usage. Second-generation biofuels could avoid many of these concerns since it relies on nonfood bioresources, such as lignocellulosics. These lignocellulosic materials are relatively inexpensive and available in large quantities. One of the most commonly examined lignocellulosic materials for second-generation ethanol production is sugarcane bagasse.[7-10]

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Table 1. Sugarcane production.

Sugarcane crops	Brazil[1]	Mexico[21,91]	Colombia[17]	Argentina[16,92]	Cuba[22,23,93]	India[25]	Thailand[15]	China[15]	World[15,17]
Year	2013	2012	2013	2010	2009	2012-2013	2013	2013	2013
Average production (million metric ton yr^{-1})	743	42.5-44.6	21.5	19	11.6	341.2-350	100.1	125.5	1877.1-1911
Average annual yield of sugarcane (metric ton ha^{-1})	120	65	108	56	22.4	70	62.6	—	—

Sugarcane is a versatile plant grown for sugar production, and its major by-product is bagasse.[1] Bagasse is the residue obtained after sugarcane is milled for juice extraction. In sugarcane production, the bagasse retrieved from crops is roughly 27–28 dry weight % of plant biomass.[1,12] It is a highly heterogeneous material that consists roughly of 20–30% lignin, and 40–45% cellulose and 30–35% hemicellulose[13] with limited amounts of extractives and ash. Its composition makes it a promising feedstock for second-generation biofuel production. Similar to other lignocellulosic materials, sugarcane bagasse has low nutritional value, which precludes concerns about the food vs. fuel debate. A variety of species of sugarcane *Saccharum* spp are grown in Latin America; this leads to numerous differing resources of bagasse, which is generally underutilized. Furthermore, bagasse represents approximately 0.3 metric ton for every 1 metric ton of sugarcane[1] grown and is often considered a waste stream. A comprehensive understanding of bagasse chemical constituents and the physical and chemical characteristic changes associated with the bioconversion process from biomass to biofuel is necessary in order to amplify bagasse as a renewable source. The delicate problem for second-generation biofuel production is the optimization of pre-treatment technologies, which may include hydrothermal, dilute acid, steam explosion, alkaline, and organosolv. Although it is costly, the pre-treatment of bagasse has been reported to facilitate up to 90% conversion of sugars to ethanol compared to 20% without pre-treatment for acid hydrolysis.[14]

Sugarcane in top producing countries

Originally from Asia, sugarcane can be found in most tropical and subtropical climates. As of 2013, the world sugarcane production accounted for approximately 1900 million metric tons with the top countries located in Latin America and Asia.[6,15] Brazil being first (~40%), India second (~19%), China third (~7%), Thailand fourth (~5%), Mexico sixth (~2.5%), and Colombia seventh (~1.5%) in global production rankings. Argentina has increased its average sugarcane growth over the last few years and now contributes to 1.1% of world production.[6] Table 1 shows the most recent approximate sugarcane crop production in different countries.

The majority of Colombian sugarcane plantations are located around the Cauca River Valley, and grow all year round with the potential to produce around 954 000 L d^{-1} of ethanol from sugarcane juice.[17] This would represent the second largest ethanol producer in Latin America with all bioethanol coming from sugarcane.[17,18] Sugarcane plantation in Cauca River Valley in Colombia is harvested on around 200 000 ha of land and it is estimated that the country can potentially generate 3.8 million L d^{-1} of fuel ethanol by 2020.[19] In Mexico, sugarcane is harvested through manual cutting once a year in a period between December and May.[20] Although Mexico is known for sugarcane crops, sugarcane yields decreased from 72 to 64 metric ton ha^{-1} annually in the last decade, which was attributed primarily to climate change.[21] Cuba used to be one of the largest exporters of sugar in the world with its main export market being the USA until the commercial trade blockage in the early 1960s. Cuba turned to the Soviet Union and Eastern European countries for trade but eventually lost these markets in 1991 due to the collapse of Communism. Since then sugarcane production has significantly declined from 80 million metric tons yr^{-1} to 24 million metric tons yr^{-1} from 1991 to 2004. In 2005 it declined to 11.6 million metric tons yr^{-1} following the trend observed in the preceding years.[22] However, Cuba has great potential for sugarcane production and energy derived from sugarcane agricultural residues is under review.[23] Argentina, on the other hand, has its production

Table 2. Characteristics of major sugarcane species.						
Reference:[6,55,94]	*S. officinarum*	*S. spontaneum*	*S. robustum*	*S. sinense*	*S. barberi*	*S.edule*
Culms thickness (cm)	3.5–6	~4	2.0–4.4	~2	~2	—
Height of plant (m)	1–6	5	10	5	5	—
Chromosome number	2n=80	2n=40-128	2n=60-~200	2n=80-124	2=111-120	2n=60-80
Classification	Noble canes	Wild species	Wild species	Ancient hybrid	Ancient hybrid	Wild species

limited to the northern, fertile, warm crop areas. Argentina typically uses the flat region in northern parts of the country, usually referred to as the Pampas, due to the very fertile land and moderate warm climate that permits year-round crop growth. Production is located on 320 000 ha of land.[16] Brazil is the leading country in sugarcane crop production with an estimated 55% of sugarcane transformed into ethanol, which yields an average of about approximately 68 liters per metric ton of sugarcane.[18] As of 2013, India is the second biggest producer of sugar in the world (27%).[24] Its cane is planted throughout three seasons (spring, summer, and fall) in the northwestern region, with 12–14 months of duration and its cultivation yielding higher amounts of cane and sugar recovery.[25] Thailand has had significant sugarcane production since 2004, a growth average of 53% from 2004 to 2013. This growth has placed Thailand as the fourth largest producer of sugarcane in the world with 51 functioning mills, 100 000 farmers on 1.6 million ha of land.[15]

Sugarcane agricultural characteristics

Sugarcane belongs to the family *Poaceae* of the genus *Saccharum*. Its taxonomy and nomenclature have been difficult to record over the years but essentially the genus *Saccharum* (S.) consisting of six species known as *S. officinarum, S. spontaneum, S. robustum, S. sinense, S. barberi,* and *S. edule*, and some of its agricultural characteristics are shown in Table 2. Among the sugarcane species, *S. officinarum* contains high sucrose; however it has poor resistance to disease. *S. spontaneum* is highly adaptable and may grow in various altitudes in tropical and subtropical climates. Due to the susceptibility to some diseases found in the most common species (*S. officinarum*), breeding methods of sugarcane have been developed. In the last three to four decades, one of the major contributions of breeding sugarcane has been to produce higher sugar yield. Hence there have been modification in sugarcane chemical composition, for example the breeding varieties from 2011 had higher lignin and ash content than that of 2009, potentially leading to lower glucose yield.[26] Currently, there are numer-

ous genetic breeding efforts such as simple sequence repeat and marker-assisted selection[27] where hybrid sugarcane plants have been derived from the crossing of *S. officinarum* and *S. spontaneum* for commercial purposes.[6,28]

Sugarcane processing

After growing for 12–16 months, sugarcane is cut for collection. Manual harvest involves burning the crop for collection, which facilitates the cutting process. This collection method is still used although many companies are projected to utilize mechanized harvesting of green sugarcane due to worker safety and environmental concerns.[29] Mechanical cutting does not involve burning the cane before collection; however it presents some operational challanges.[29] It has been highly adopted since it replaces the labor of up to 100 workers per farm in manual harvest.[30] In most recent studies, the state of São Paulo in Brazil used the green-harvest system for the cane, which accounted for 65.2% of the harvesting method and is expected to banish the burning harvest by 2029.[31] Mechanical cutting does not permit the cane to be washed because the loss of sucrose is higher; hence mills use a dry wash process (i.e., jets of air). The chopped sugarcane is then placed in a shredder with the objective of opening the cells containing sugars and facilitating the sucrose extraction process. Grinding is an extraction process, which results in juice extraction and the agriculture residue, bagasse. Usually the first batch of juice extracted goes to sugar manufacturing and about 55%[32] goes to ethanol production. Sugarcane is usually cultivated for six years before replanting.[20] Sugarcane maturity, harvesting method, type of soil, and efficiency of equipment used for the extraction process may affect the composition of sugarcane bagasse.

Pre-treatment of sugarcane bagasse

The conversion of bagasse to biofuels has been actively studied using both the biological and thermal platform. One of the most promising pathways is second-generation
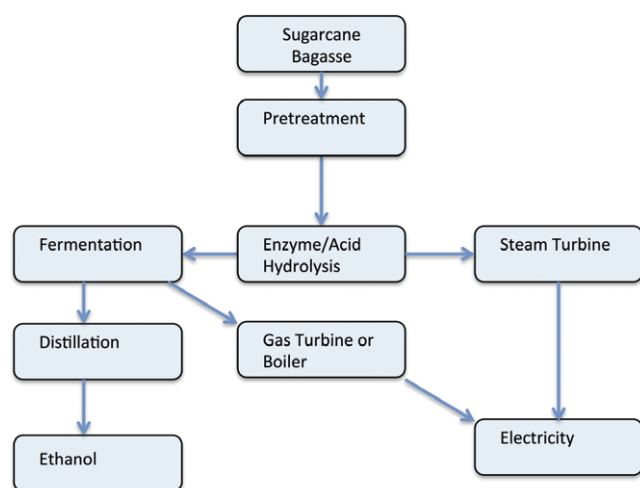
Figure 1. Schematic for bioethanol and biopower for sugarcane bagasse.

Table 3. Different pre-treatment conditions for sugarcane bagasse.

Pre-treatment	Operating Conditions	Reference
Steam explosion	0.6–4.8 MPa, 160–260°C, 15 min	33, 95
Hot water	120–230 °C, 1–80 min	37–39, 83
Alkaline	53.2–120 °C, 4–65.6 h	33, 46
Organosolv	150–200°C, 30–90 min, 35–70% of solvent	33, 37, 45, 83
Dilute acid	100– 120 °C, 40–120 min, 1.8–10% of acid concentration	42, 96
Concentrated acid	80 °C, 90 min, 18–40% of acid concentration	42
Ionic liquids	60–140 °C, 5–360 min, 3–10% of solvent	48, 50–52
Dilute acid (1) + microwave heat (2)	(1) 1.56% of acid concentration, 0.2M, pH 0.68 (2) 130–190 °C, 5–10 min, 2.45 GHz, 900 W	41

cellulosic ethanol as summarized in Fig. 1. Pre-treatment is one of the major steps in the biological conversion of bagasse to bioethanol as it reduces its recalcitrance. It can be accomplished using biological, chemical, physical, or various combinations of these treatments. The reduction in recalcitrance has been attributed to several factors including changes in the interactions of hemicellulose, cellulose, and lignin; increases in cellulose accessibility; removal of lignin-carbohydrates complexes; and possible reductions in cellulose crystallinity in the plant cell wall. These effects increase sugar yields from cellulose thereby increasing ethanol fermentation yields provided fermentation inhibitors are managed. A variety of pre-treatments have been used in recent studies for sugarcane bagasse as summarized in Table 3.

Steam explosion is a physico-chemical pre-treatment prevalently used in sugarcane industry due to its low environmental impact and cost.[8,33] It is a process in which the lignocellulosic materials in sugarcane bagasse are exposed to hot steam and pressure followed by explosive decompression of bagasse that results in lignin rearrangement due to partial hemicellulose hydrolysis and lignin solubilization due to high temperatures.[34] Enzymatic hydrolysis is also facilitated by changes in cellulose crystallinity and degree of polymerization caused by steam explosion.[35]

Hot water pre-treatment of bagasse is environmentally beneficial as there is reduced deterioration of polysaccharides, and consequently lower inhibitor generation.[36] The disadvantage to this pre-treatment is the high volume of water consumption and energy costs. This method generally employs temperatures ranging from 120 to 230 °C for 1–80 min and may recover 55 to 84%

of hemicelluloses.[37–39] However, shorter periods of time ranging from 1 to 20 min and temperatures lower than 200°C are more commonly used so to minimize changes in lignin and cellulose.

The extrusion process is a physical pre-treatment method that utilizes irradiation, and comparable to other treatments, targets the degradability of lignocellulosic materials for the enhancement of enzymatic hydrolysis. Such irradiation treatment for sugarcane bagasse comes in the form of microwaves, ultrasound and gamma rays.[33,40] Gamma rays increase cellulose crystallinity as well as surface area, whereas microwave and ultrasound irradiation, given adequate conditions, decrease crystallinity of cellulose.[33,40,41]

Acid hydrolysis is efficient in breaking down hemicellulose and maximizes sugar yield from bagasse. It is a commercial method adopted by many researchers however the cost is claimed to be higher than that of liquid hot water pre-treatment.[37] Dilute acid and concentrated acid are two types of acid hydrolysis. Dilute acid usually uses less than 10% acid concentration while concentrated acids is greater than 10%.[42] Acids such as sulfuric and phosphoric acid help to solubilize hemicelluloses and transform them into fermentable sugars.[43] In sugarcane bagasse pre-treatment using sulfuric acid with 0.5% concentration at 121°C during 60 min yielded 24.5 g L^{-1} of total sugar after cellulose hydrolysis.[13] The use of hydrochloric acid has also been studied at 130°C, 1.25% HCl concentration for 10 min resulting in 76.6% sugar release after 72 h of enzymatic hydrolysis.[44]

Organosolv pre-treatment of sugarcane bagasse mainly utilizes ethanol (EtOH) and water as an organic solvent mixture.[33] The α-aryl ether linkages of lignin are reactive under these conditions and are hydrolyzed and solubilized. This process is convenient for small mills because of its ease of recovery method and sulphur free discharge[37] but remains costly.[33] When bagasse was mixed with 60:40 EtOH/water with 5% dosage of acetic acid at 190°C for 45 min, sugar yield reached 85.4% after 72 h of enzymatic hydrolysis.[45]

Alkaline pre-treatments of bagasse promote the separation of cellulose and are efficient in the removal of lignin. The alkali usually causes a swelling in the biomass, which allows for the decrease in cellulose crystallinity. In contrast to other pre-treatments, this particular process works at low reaction pressures, temperatures and concentration, which can be linked to reduce fermentation inhibitors and low cost.[46] However, its biggest disadvantage is associated to the difficulty of alkali recovery. A sodium hydroxide pre-treatment (i.e., 110°C for 1 h and 0.18% of NaOH) of bagasse has been shown to result in 77.3% sugar release after 72 h of enzymatic hydrolysis.[44]

Ionic liquids are salts composed of anions and cations of organic compounds, which are poorly organized making them have a melting point below 100 °C.[47] These solvents have great thermal stability and non-volatility[48] and are exceptional catalysts for the delignification of bagasse.[49] Among different ionic solvents, most commonly used for sugarcane bagasse is 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]), which has been reported to be very effective in dissolving cellulose.[50] Other solvents used for pre-treatment of bagasse that have been reported include 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]), 1-allyl-3-methylimidazolium chloride ([Amim][Cl]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1,3-dimethylimidazolium dimethyl phosphate ([Mmim][DMP]).[48,51,52] These ionic liquids can remove up to 60% of lignin in sugarcane bagasse along with decreasing the crystallinity of cellulose fibers.[53] It has been reported that a 1:20 solution of bagasse to ([Mmim][DMP]) at 120 °C for 120 min resulted in 70.38% of sugar conversion after 48 h of enzymatic hydrolysis.[52]

Sugarcane bagasse constituents and characteristics

Cellulose structure

Cellulose is a homopolysaccharide chain composed of anhydroglucose units linked by β-(1,4)-glycosidic bonds (Fig. 2) which form a crystalline structure due to extensive
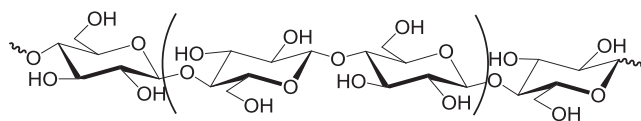

Figure 2. Structure of cellulose.

intra- and intermolecular hydrogen bonds that facilitates its aggregation into fibrils.[54] The average molecular weight of sugarcane bagasse cellulose ranges from 157 800- to 168 400g mol[1; 50] and the size of its cellulose fibers range from 1.0 to 1.5 mm.[55] A cellulose unit, known as elementary fibril undergoes self assembly to form micro-fibrils, which can then be cross-linked by hemicellulose matrices to form macro-fibrils, which creates resistance to chemical and enzymatic degradation.

Degree of polymerization pertains to the number glucose units in the molecular polymer and it can influence the effectiveness of enzymatic hydrolysis. The average degree of polymerization (DP_w) in sugarcane bagasse cellulose ranges from 974 to 1039.[50] DPw varies under different cellulose isolation methods and is dependent on the intrinsic viscosity (η). Intrinsic viscosity is the measure of volume occupied by the macromolecule and their ability to disturb flow (Table 4).[56] When sugarcane bagasse was subjected to delignification and potassium hydroxide isolation the DP_w was 1406.5 while the combination of acetic and nitric acid lowered DP_w to 822.5, indicating that the acetic and nitric acid mixture degrades the macromolecule of cellulose more than potassium hydroxide.[56]

The predominant polymorph of cellulose is known as cellulose I and can be detected through X-ray diffraction (XRD) and solid state cross polarization magic-angle spinning carbon-13 nuclear magnetic resonance (CP/MAS ^{13}CNMR) spectroscopy.[56] XRD is one of the most commonly used techniques for crystallinity index (CrI, %) analysis[57,58] and it showed that the untreated bagasse contains an average CrI of 56.7%. Table 4 shows the CrI of untreated commercial sugarcane bagasse. This index is frequently used to determine relative quantity of crystalline material present in sugarcane bagasse. CP/MAS[13]CNMR has shown to be extremely resourceful in the morphological modifications analyzed in cellulose throughout hydrolysis, where the 64.8 ppm chemical shift corresponds to the C-6 crystalline cellulose signal and this is ratioed to 62.4 ppm signal for the C-6 amorphous of cellulose.[56]

Hemicellulose structure

Hemicellulose is a heteropolysaccharide of low molecular weight. It averages 7380g mol[1] in bagasse.[59] Sugar

Table 4. Degree of polymerization of isolated cellulose of sugarcane bagasse and crystallinity index of commercial type bagasse.

	Cellulose of sugarcane bagasse				
	Cellulose A[a,56]	Cellulose B[b,40]	Cellulose C[97]	Cellulose D[98]	Cellulose E[99]
DP_w	822.5–1406.5	1858.1–2040.8	1277.0	1309.6	1356.0
Intrinsic Viscosity (η, ml g^{-1})	256.3–415.6	534.1–631.6	378.0	387.2	399.5[c]
Molecular Weight (M_w, g mol^{-1})	133250–227850	301000–362600	206800	212150	Not reported
	Sugarcane bagasse commercial variety				
	SP79–1011[57]	RB867515[57]	SP81–325[57]	RB92579[57]	Bagasse E[99]
CrI %	52.7	55.8	52.6	60.4	62.0

[a,b] range of 6 isolated cellulose of bagasse under different isolation conditions.
[c,56] intrinsic viscosity (η) calculated from $DP_w^{0.9}=1.65(\eta)$

Table 5. Content of neutral sugars and uronic acids of isolated hemicellulose from sugarcane bagasse.

Isolation of Hemicellulose	Xylose (%)	Arabinose (%)	Glucose (%)	Galactose (%)	Mannose (%)	Rhamnose (%)	Uronic Acids (%)
Dewaxed + distilled water[59]	55.20	10.73	20.42	7.68	4.13	1.84	6.95
NaOH[59]	81.37	11.93	3.97	1.78	0.47	0.48	3.50
NaOH + H$_2$O$_2$[59]	85.02	8.65	5.87	0.46	Trace	Not detectable	1.75
H$_2$O[a, 61]	57.43	6.25	28.52	6.36	—	—	1.44
H$_2$O + KOH[a, 61]	79.92	5.5	12.03	0.88	—	—	1.67
KOH[b, 68]	83.1–84.6	11.0–12.1	2.1–3.1	0.5–0.7	—	—	1.4–2.6
H$_2$O$_2$[c, 67]	73.1–82.6	3.8–7.2	3.8-7.9	—	—	—	3.6–7.0

[a] precooked with H$_2$O$_2$ and MgO.
[b] range composition of 7 isolated hemicellulose.
[c] range composition of 19 isolated hemicellulose.

composition of hemicellulose in bagasse is primarily galactose (11.5–39.9%), xylose (15.5–28.9%) and glucose (17.5–50.5%) with smaller amounts of arabinose (5.35–14.31%), mannose (0.0–14.0%), rhamnose (2.5–10.6%) and uronic acids (1.0–2.3%).[60] Hemicellulose in sugarcane bagasse is composed of β-(1,4)-xylo-pyranose backbone, having about 200 β-xylopyranose residues linked by 1,4-glycosidic bonds, glucomannas and galactomannans, xyloglucans, β-glucans and small amounts of uronic acids.[61,62] The degree of branching in hemicellulose is given by the arabinose/xylose ratio; hence, the lower the ratio the higher the degree of polymerization and likewise the higher the ratio the shorter the polymer chain.[60] Values for the arabinose/xylose ratio are approximately 0.2 for bagasse.[59, 63] Hemicellulose is linked to lignin by covalent bonds, whereas the linkage between hemicellulose and cellulose is by the way of hydrogen bonds,

which integrate easily with one another creating stability and flexibility.[64] In sugar cane the hemicellulose content is found to be low, on average 19.90%,[65] compared to that of sugarcane bagasse which is approximately between 30 and 35%.[13] There are many methods of extraction of hemicellulose such as autohydrolysis,[66] active oxygen species (oxygen and hydrogen peroxide) and solid alkali,[61] and alkaline peroxide.[67,68] In general, isolation comes from multiple alkaline extractions causing the cleavage of ester linkages and extracting the hemicellulose from the lignocellulosic matrix. Potassium hydroxide and sodium hydroxide with hydrogen peroxide pre-treatments for hemicellulose isolation have shown high values for xylose, 83.1–84.6 and 85.02%, respectively.[59,68] In comparison, dewaxed and distilled water, and water with solid alkali precooking resulted in much lower xylose yields, 55.20 and 57.43%, respectively (Table 5).[59,61]
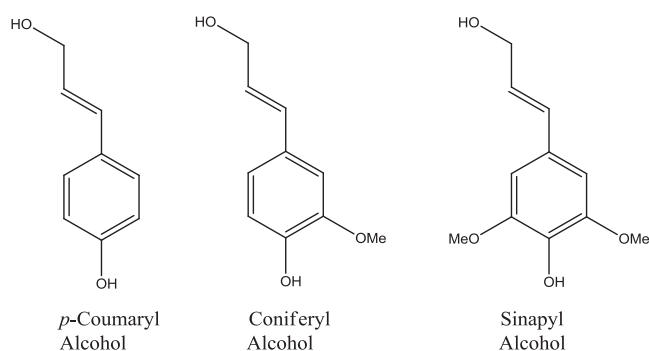
Figure 3. Typical monolignols.

Structural changes in bagasse hemicellulose after isolation are typically analyzed using Fourier transform infrared spectroscopy (FTIR) and ^{13}C NMR. [59, 61, 63] FTIR has indicated complete rupture of ester bonds when under alkali pre-treatment conditions (10% potassium hydroxide with 20°C, 35°C and 50°C). [68] ^{13}C NMR was able to detect strong signals indicating the presence of 1,4-linked b-D-Xyl p units and the 4-O-methoxyl group of glucuronic acid residues in xylan. [59,61] It was concluded that b-D-Xyl p units was the main component in bagasse hemicellulose. [61]

Lignin structure

Lignin, the most abundant aromatic polymer, is an amorphous three-dimensional phenolic biopolymer. The biosynthesis of lignin could be considered to arise from polymerization of three types of phenylpropane units as the monolignols: p- coumaryl, sinapyl and coniferyl alcohols that allows for the rigid form (Fig. 3). These monolignols can then give rise to the p-hydroxyphenyl (H), syringyl (S), and guaiacyl (G) lignins units. [51] Lignin in bagasse has a molecular weight average range of 507–3973 mol g^{-1} [69] Lignin in sugarcane is extremely low, average of 2.37% [70] and 4.16%, [65] compared to ~25% found in sugarcane bagasse. Additionally, it has been reported that lignin content in sugarcane genotype IACSP04-627 to be 8.12% and IACSP04-065 to be 4.32%. [71] Table 6 shows the lignin content in different sugarcane bagasse.

Lignin affects most pre-treatment methods as well as enzymatic hydrolysis, thus multiple studies have been made for structural information of lignin, such as ionic liquid, ammonia, dilute acid, etc. [51,56] Characterization methods for bagasse such as pyrolysis coupled to gas chromatography mass spectrometry (Py-GC-MS) showed that both coumaric and ferulic acid play an important role in the structure of bagasse. [72–74] The g-OH acylation of lignin side-chain by r -coumarates indicating that

Table 6. Lignin content in sugarcane bagasse from different variety of sugarcane.			
	Lignin content in sugarcane bagasse (%)		
Sugarcane variety	Klason lignin	Acid-soluble lignin	Total lignin[a]
Hybrid 140[100]	—	—	21.5 ± 0.2
Hybrid 321[100]	—	—	20.2 ± 0.4
Hybrid 58[100]	—	—	18.6 ± 0.1
Hybrid 146[100]	—	—	18.6 ± 0.1
Hybrid 89[100]	—	—	16.8 ± 0.1
PE-BR[b,101]	—	—	21.1 ± 0.9
NA-BR[c,9]	19.7 ± 0.1	2.2 ± 0.2	21.9 ± 0.3
Raw bagasse[69]	25.9 ± 0.3	4.7 ± 0.3	30.6 ± 0.6
Raw bagasse B[102]	22.9 ± 0.7	0.06 ± 0.0	23.0 ± 0.7
RB867515[72]	17.8 ± 0.6	2.2 ± 0.2	20.0 ± 0.8

[a] sum of klason and acid-soluble lignin.
[b] sugarcane bagasse from Pernambuco - Brazil.
[c] sugarcane bagasse from Nova America - Brazil.

r -coumarates are primarily attached to the lignin polymer. Ferulates however, showed acylation of arabinosyl residue from arabinoxylan chains revealing that ferulates are generally linked to carbohydrates in the cell-wall. [72] Ionic liquid and hot water pre-treatment both hydrolyzed the b-O-4 inter-unit links. [51,69] Different methods for lignin isolation in sugarcane bagasse were efficient for lignin extraction processes showing the cleavage of b-O-4' linkages such as: dilute acids followed by steam explosion and ethanol washing, as well as alkali followed by steam explosions. [69] Proton, carbon, phosphorus and two-dimensional heteronuclear single quantum coherence nuclear magnetic resonance (^{1}H, ^{13}C, ^{31}P and 2D HSQC NMR) are primarily used to identify the functional groups in the isolated lignin structure. [51,69] An assessment of various hydroxyl groups in organosolv lignin, with results S-OH: 0.58 mmol g^{-1}, G-OH:0.47, H-OH:0.53 among others, can be obtained using ^{31}P NMR spectra. [75] The 2D HSQC NMR is able to approximately determine the carbohydrate complexes of lignin that ^{1}H, ^{13}C and ^{31}P NMR are not able to detect due overlapping in signals. [51] Isolated lignin from sugarcane bagasse was reported to be composed of 83% of b-O-4' links, alkyl-aryl ether bonds, and very few quantities, 6% of b-5, phenylcoumarans; and, molar ratio of H:G:S was confirmed to be 2:38:60 respectively, [72] concluding bagasse is S-rich (Table 7). According to del Río et al. [8] the lignin of bagasse is derived from mature stem and

Table 7. S:G:H ratio of lignin in sugarcane bagasse.

Lignin aromatic units	Ball milled lignin[69]	Ethanol lignin[69]	Water soluble lignin[69]	Dioxane lignin[69]	Ball milled 2 lignin[72]	Whole cell wall lignin[72]
S (%)	55.4	58.4	53.6	55.0	60.0	60.0
G (%)	39.1	30.5	32.5	38.3	38.0	37.0
H (%)	5.5	11.1	13.9	6.7	3.0	2.0
S/G ratio	1.4	1.9	1.6	1.4	1.6	1.6
r -coumarate/ferulate ratio	9.8	4.5	1.9	6.2	2.6	12.0

therefore is rich in syringyl (S) lignin, which is present in mature tissue. The conclusions indicated that lignin from sugarcane bagasse is mainly composed of β-O-4' alkyl-aryl ether linkages.

Ash and extractives

The by-product of sugarcane bagasse after it is used for fuel in plants cogeneration systems is bagasse ash. Sugarcane bagasse ash is black in color and contains 2.39 g cm^3 of particle density with irregular shaped particles.[76] It contains about 87.8% of sand with particles sizes greater than 63 μm, 11.50% of slit with particles sizes ranging from 2 to 63 μm, 0.7% of clay with less than 2 μm and 10.32% of organic matter.[76,77] In Brazil, sugarcane bagasse ash generation was estimated to be approximately 2.5 million tons per year and is discarded primarily as soil fertilizer.[77] Economical and technological development for the application of ash have grown in the past few years. Ash from bagasse is rich in silica and hence may be used for recycling purposes such as ceramic raw material, additive to cement, concrete and fine aggregate in mortars.[77,78] X-ray

diffraction (XRD) has been used to determine the inorganic oxide content in bagasse ash (Table 8).[76–78]

Extractives in sugarcane bagasse range from 2.3 to 10.5% of total chemical composition.[79] These extractives are hydrophobic and can be fatty acids, waxes, and proteins, among others.[79,80] Research has reported that about 0.9% of acetone extractives contained about 140 mg k^{-1}g of n-fatty acids, 700 mg k^{-1}g of n-aldehydes and 330 mg k^{-1} of n-fatty alcohols in bagasse.[79] For chemical analysis purposes, extractives are usually removed from sugarcane bagasse. However, extractives may be a great source of value in major-scale biorefineries for cellulosic ethanol production from bagasse.[9]

Biomass to bioethanol

Efficient hydrolysis of the sugarcane bagasse along with the subsequent fermentation of sugars creates a compelling commercial opportunity. According to Lino et al.,[81] sugarcane encompasses two-thirds of the production of sugar in the world. The advantages of biorefining sugarcane bagasse to bioethanol would include an ease of production when integrated into a sugarcane ethanol existing mill, hence lowering any necessary investments.

Sugarcane bagasse to bioethanol

A study presented by Walter et al. showed that if 76% of bagasse is pre-treated and enzymatically hydrolyzed for sugar, this sugar could be fermented to yield up to 149.3 liters of ethanol per ton of bagasse.[82] Other studies suggest that in a two step pre-treatment using a dilute acid pre-treatment condition at 175°C for 40 min and 1% H_2SO_4 concentration with a 1:1 solid liquid ratio, followed by an organosolv treatment, it is possible to achieve 192 liters of ethanol per ton of bagasse. Whereas using similar conditions, 120°C for 40 min with 1% H_2SO_4 concentration with a 1:4 solid liquid ratio followed by organosolv, ethanol generation could produce up to 180 liters of per ton of sug-

Table 8. Chemical characteristics of sugarcane bagasse ash.

(%)	Bagasse ash 1[77]	Bagasse ash 2[103]	Bagasse ash 3[76]	Bagasse ash 4[78]
SiO_2	61.59	72.95	85.55	80.2
Al_2O_3	5.92	1.68	2.29	2.60
Fe_2O_3	7.36	1.89	1.21	5.60
K_2O	6.22	9.28	1.33	4.00
CaO	5.00	7.77	4.05	1.80
MnO	0.10	—	0.08	0.20
TiO_2	1.46	—	0.20	1.40
SO_3	0.42	4.45	2.28	0.10
MgO	1.17	1.98	—	1.60
P_2O_5	0.98	—	3.01	1.40

arcane bagasse.[83] Different pre-treatments and pathways for hydrolysis and fermentation have varying effects on glucose concentration available for fermentation contributing to different ethanol production (Table 9).

Cogeneration systems are very common in sugar mills.[23, 84] When using cogeneration systems for first and second generation production simultaneously in different boiler pressures (2.2–9.0 MPa), it was shown that the system using 2.2 MPa achieved a maximum yield of anhydrous ethanol production of 113.7 liters per ton of sugarcane.[85] According to Dias et al.[86] the double-effect distillation process of sugarcane bagasse is compared to conventional distillation. In the double-effect process, the distillation columns operates under vacuum pressures ranging from 19 to 25 kPa and the rectification columns pressure ranges from 101 to 135 kPa with an extractive distillation process using monoethyleneglycol (MEG) for ethanol dehydration, providing higher yields of anhydrous ethanol from bagasse than conventional (Table 10). Hemicellulose pentoses, mainly xylose and arabinose, are difficult to transform for the production of second-generation bioethanol, hence metabolic microorganisms are necessary to succeed on pentose.[66] Thus, pre-treatment of bagasse is necessary in order to modify chemical composition, size and structure in such manner in which hydrolysis can be carried out promptly and with increased yields.

Biomass to biopower

Power generation in the world is another cause of increased pollution and climate change. Countries are seeking renewable energy sources for electricity production for the foreseeable future. In 2009, the Energy Information Administration (EIA) compared renewable electricity to net generation (Table 11) of the top five countries. Although China and the USA are the leading net power generation countries, at 576.605 and 429.652 billion kWh respectively, currently, their renewable power energy profiles are less than 17% of the electricity generated. By contrast, Brazil and Canada have been more successful regarding renewable energy, producing 89.6% and 63.3%, respectively of the total energy produced from renewable sources, chiefly hydroelectric power.

Cogeneration systems generate electricity and thermal energy at high output capacities. In 2004 Cuba reached 600 MW of cogeneration capacity in the 85 sugarcane mills active.[22,23] If 45 of the active 85 mills, which has a capacity of 4600–14000 ton of cane a day, were modernized cogeneration capacity would increase substantially to 1400–1600 MW.[22]

Table 9. Ethanol yield from fermentation of SHF and SSF under different pre-treatments.

Bagasse pre-treatment	Parameters		
	Initial glucose concentration (g L^{-1})	Ethanol produced (g L^{-1})	Ethanol yield (%, ethanol produced by gram of glucose)
Separate hydrolysis and fermentation (SHF)			
SEB^{a,102}	57.7 ± 1.4	25.6 ± 0.3	44.4
SA-AWB6^{b,102}	50.1 ± 0.2	23.4 ± 0.2	46.6
SA-AWSEB^{c,102}	50.1 ± 1.4	20.4 ± 0.1	40.8
AH^{d,9}	57.8	25.2	43.6
H$_3$PO$_4$^{9}	54.9	24.9	45.4
H$_2$SO$_4$^{9}	54.9	20.1	43.7
Simultaneous saccharafication and fermentation (SSF)			
AH$^{d, 9}$	54.9	18.8	34.2
H$_3$PO$_4$^{9}	53.4	16.9	31.6
H$_2$SO$_4$^{9}	48.2	18.4	37.2

^{a} Steam-exploded bagasse.
^{b} Sono-assisted alkali-washed bagasse.
^{c} Sono-assisted alkali-washed steam-exploded bagasse.
^{d} Autohydrolysis (Liquid hot water) bagasse.

Table 10. Sugarcane juice and bagasse results from conventional and double-effect distillation processes.

Reference:[86]	Conventional distillation	Double-effect distillation
Anhydrous ethanol from bagasse (L t^{-1} cane)	18.8	22.0
Anhydrous ethanol from sugarcane juice (L t^{-1} cane)	83.7	83.7

Table 11. Top 5 countries in electricity generation and its renewable use.

Reference[1]	Generated electricity (billion kWh)	Renewable electricity %
China	576.605	16.7
USA	429.652	10.9
Brazil	410.258	89.6
Canada	371.008	63.3
Russia	165.227	17.8
World	3760.590	—

Sugarcane bagasse to biopower

Sugar and ethanol plants often utilize sugarcane bagasse as a source of fuel because it can produce enough power and heat to meet all needs. These plants are self-sufficient

Table 12. Electricity productions in BPST and CEST system.

System	BPST			CEST		
Condition of turbine	1.9MPa, 593K (7MW)[23]	2.2–10MPa, 573–803K[88]	6.0MPa, 754K[104]	4.2MPa, 693K (38MW)[23]	6.3MPa, 793K (30MW)[23]	6.5–10MPa, 753–803K[88]
Electricity generated (KWh t^{-1} cane bagasse)	22.79	38.62–99.51	114.00	110.00	130.00	105.48–121.22
Electricity surplus (KWh t^{-1} cane bagasse)	—	10.62–71.51	90.20	85.00	105.00	77.48–93.22

in energy consumption and often still have a surplus of bagasse which can present environmental concerns due to its prolonged on site accumulation, which poses a threat for spontaneous combustion.[87] The mills in Brazil generate on average 12kWh of electricity per ton of sugarcane bagasse, 330 kWh of heat energy and 16kWh of mechanical energy.[84]

Steam-based sugarcane mills can be found in countries like Cuba and Brazil, which utilizes two types of steam turbines for low pressure steam and electricity production: Condensing Extraction Steam Turbine (CEST) and Backpressure Steam Turbine (BPST).[23,88] CEST are high-pressure turbines used in sugar factories that are favored for pressure levels above 65 bar.[89] Any accessible residue from sugarcane processes such as lignocellulosic biofuel would be implemented for generating electricity. BPST, on the other hand, are non-condensing turbines, commonly found in refineries, in which exhaust steam at lower pressure loads and are usually cheaper than condensing turbines. BPST could generate up to 99.51 kWh per ton cane and fulfill electricity demand at the mills, while CEST could generate 121 kWh per ton cane, meet the energy demand at the mills and would export the surplus electricity, approximately 93 KWh per ton cane for public use (Table 12).[88] Alves et al.[88] also revealed that CEST yielded a surplus of electricity, unlike BPST because all available bagasse is consumed as fuel.

Gasification and Fischer-Tropsch (GFT) conversion process for sugarcane bagasse has been studied and concluded to be effective in energy efficiency for both liquid fuel production and overall energy when compared to other conversion process such as acid or enzymatic hydrolysis and saccharification and fermentation processes.[82,83] Research studies by Walter et al.[82] using sugarcane residues, trash, and bagasse were analyzed for production of ethanol and electricity in terms of hydrolysis and gasification and Fischer-Tropsch processes. Multiple variables to avoid emissions of greenhouse gas emissions were hypothesized and it was concluded that GFT was slightly more feasible and effective where the estimated avoided emissions was

263.9 kg CO_2 equivalents per ton of carbon, with 67% from conventional ethanol production and 11% from surplus electricity production. While the same variables were taken into consideration in the hydrolysis process, the avoided emission was estimated to be 253.2 kg CO_2 equivalents per ton of carbon, with 94% from ethanol production and 6% from surplus electricity production. Another study determined that the avoided carbon dioxide emissions were larger for maximum ethanol production than that of the electricity production, concluding that a plant in which produces ethanol is more desirable then a plant that produces electricity using bagasse in order to avoid CO_2 emissions.[90] These processes are still under development and it is unknown which method is superior or more feasible and cost effective for a commercial scale.

Conclusions

Sugarcane is one of the most abundant crops in the world having innumerous mills and plants for sugar extraction and first-generation ethanol production. Most Latin American countries possess tropical climates enabling them to generate sugarcane crops. Brazil alone is the greatest sugarcane producer utilizing ethanol for the majority of its cars sold, followed by Mexico and Colombia, and other countries with great potential for both bioethanol and biopower growth. Bagasse is a promising agricultural residue in bioethanol production and power generation due its high cellulose and average lignin and hemicellulose content.

Pre-treatment is one of the most crucial steps for ethanol production. Although there is not a specific pre-treatment that is most used for commercial purposes and is cost-effective, the appropriate method of pre-treatment followed by acid or enzymatic hydrolysis and fermentation is important for high yields in the conversion of sugars to ethanol. Commonly used are steam explosion, which is used for partial hemicellulose hydrolysis and lignin rearrangement; and dilute acid, which transforms a solubilized portion of hemicellulose into fermentable sugars. Similarly

in power generation, specific processes have not been utilized in a commercial scope, CEST turbines and GFT conversion method appear to be promising due to its higher surplus electricity and hence energy efficiency.

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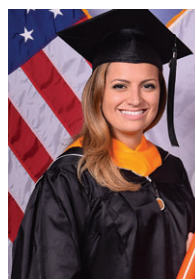
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